

AD-A268 962 ITATION PAGE

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OMB No. 0704-0188

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1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE

July 15, 1993

3. REPORT TYPE AND DATES COVERED

scientific reprint 1990-92

4. TITLE AND SUBTITLE

Determination of Hyperfine Splittings of Biradical Termini  
by Combining Biradical Trapping and Time-Resolved ESR  
Techniques

5. FUNDING NUMBERS

61102F 2303 B2

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Columbia University  
Box 20, Low Memorial Library  
New York, NY 10027

8. PERFORMING ORGANIZATION  
REPORT NUMBER

3 0001

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AFOSR/NC  
Building 410, Bolling AFB DC  
20332-6448

10. SPONSORING/MONITORING  
AGENCY REPORT NUMBER

AFOSR-91-0340

11. SUPPLEMENTARY NOTES

The Journal of Physical Chemistry, vol. 97, pp. 7247-7252 (1993).

12a. DISTRIBUTION/AVAILABILITY STATEMENT

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED

83

8

31

042

93-20322



13. ABSTRACT (Maximum 200 words)

ESR detection of spin-polarized short-lived biradicals has been shown to be a valuable tool in studying the mechanisms of photochemical reactions and in the investigation of the properties of biradicals. However, some important spectroscopic features of these species are not readily available because of certain peculiarities of biradical ESR spectra. This difficulty can be overcome through the conservation of spin polarization by the controlled scavenging of a biradical into a subsequent radical species whose spectroscopic features can be accurately evaluated. In particular, it is shown that the hyperfine splittings of a radical site in a biradical can be measured directly by time resolved ESR if the other site is scavenged by a selective spin trap.  $\text{BrCCl}_3$  was used as a selective scavenger of the acyl moiety of polymethylene linked acyl-alkyl and acyl-benzyl biradicals formed in the photolysis of substituted cycloalkanones in solution. Transformation of these polarized biradicals into corresponding polarized monoradicals upon bromine abstraction by acyl site leads to much less complicated and much better resolved ESR spectra. The hyperfine splittings of the benzylic termini of several acyl-benzyl biradicals generated in this manner were evaluated and quantitatively compared with the splittings of benzyl and 1-phenylpropyl radicals formed in the

14. SUBJECT TERMS

biradicals; time-resolved ESR; photolysis; cycloalkanones

15. NUMBER OF PAGES

6

16. PRICE CODE

17. SECURITY CLASSIFICATION  
OF REPORT

unclassified

18. SECURITY CLASSIFICATION  
OF THIS PAGE

unclassified

19. SECURITY CLASSIFICATION  
OF ABSTRACT

unclassified

20. LIMITATION OF ABSTRACT

none

photolysis of linear ketones.

# Determination of Hyperfine Splittings of Biradical Termini by Combining Biradical Trapping and Time-Resolved ESR Techniques

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Received: March 5, 1993; In Final Form: April 26, 1993

ESR detection of spin-polarized short-lived biradicals has been shown to be a valuable tool in studying the mechanisms of photochemical reactions and in the investigation of the properties of biradicals. However, some important spectroscopic features of these species are not readily available because of certain peculiarities of biradical ESR spectra. This difficulty can be overcome through the conservation of spin polarization by the controlled scavenging of a biradical into a subsequent radical species whose spectroscopic features can be accurately evaluated. In particular, it is shown that the hyperfine splittings of a radical site in a biradical can be measured directly by time resolved ESR if the other site is scavenged by a selective spin trap.  $\text{BrCCl}_3$  was used as a selective scavenger of the acyl moiety of polymethylene linked acyl-alkyl and acyl-benzyl biradicals formed in the photolysis of substituted cycloalkanones in solution. Transformation of these polarized biradicals into corresponding polarized monoradicals upon bromine abstraction by acyl site leads to much less complicated and much better resolved ESR spectra. The hyperfine splittings of the benzylic termini of several acyl-benzyl biradicals generated in this manner were evaluated and quantitatively compared with the splittings of benzyl and 1-phenylpropyl radicals formed in the photolysis of linear ketones.

## Introduction

Transient biradical species have been the subject of considerable interest for quite a long time.<sup>1</sup> Spin trapping is a commonly employed technique to establish the identity of biradicals and to evaluate such parameters as their lifetimes<sup>2,3</sup> and even singlet-triplet splittings.<sup>4</sup> Biradical scavenging was also shown to alter the relative yields of intramolecular products<sup>2,5</sup> as well as the efficiency of  $^1\text{H}$  and  $^{13}\text{C}$  nuclear spin polarization (CIDNP) and  $^{12}\text{C}/^{13}\text{C}$  isotope separation in the products of biradical reactions.<sup>6-8</sup> Paramagnetic scavengers, such as free radicals<sup>9-11</sup> or molecular oxygen,<sup>3</sup> are able to assist intersystem crossing in biradicals. However, reactions of diamagnetic quenchers with biradicals often resemble those with the corresponding monoradicals.<sup>12,13</sup> Thus, the result of scavenging of biradicals by diamagnetic scavengers can usually be predicted if the reactivity of monoradical analogs is known.

Until recently, the direct observation of biradicals by electron spin resonance (ESR) spectroscopy was successful only under conditions which made biradicals relatively stable, e.g., by the matrix isolation technique.<sup>14</sup> The development and application of direct detection time resolved ESR (TR ESR) has allowed the thorough investigation of the ESR spectra of short-lived polymethylene linked acyl-alkyl and bis(alkyl)biradicals formed in the photolysis of methyl substituted cycloalkanones.<sup>15-17</sup> In particular, the parameters for exchange interaction of electron spins for biradicals of different chain lengths including the cases with restricted chain flexibility were evaluated.<sup>18</sup> The relative contributions of through-bond and through-space couplings in biradicals are also issues of current interest.<sup>19</sup>

To clarify further the mechanisms of exchange interaction and to refine the exchange parameters extracted from the simulations of TR ESR spectra, it is useful to investigate a range of biradicals of different structures.<sup>20</sup> As an extension of investigating their photochemistry, we are currently studying the polarized ESR spectra of acyl-benzyl and bis(benzyl) polymethylene linked biradicals formed in the photolysis of 2-phenyl- and 2,2-diphenylcycloalkanones by the TR ESR technique.

[Preliminary results were reported: Koptuyg, I. V.; Turro, N. J. *International Symposium on Magnetic Field and Spin Effects in Chemistry*; Konstanz, Germany, 1992.] As has been shown,<sup>16</sup> the information of interest, such as the exchange parameters, can only be reliably recovered through a comparison of experimental results with model calculations which, in turn, require accurate knowledge of hyperfine coupling (HFC) constants and g-factors of the biradical termini; and while it is the ESR technique which usually provides this information, the biradical nature of the intermediate usually prevents the accurate evaluation of the hyperfine splittings because of the complexity of the spectra of biradicals (*vide infra*). A common approach in overcoming this problem is to use the hyperfine splittings of structurally similar monoradicals in computing the spectra of biradicals. However, appropriate model monoradicals are not always available, as in the case of 1-phenylalkyl radicals, and models which are available are often studied under different experimental conditions (solvent, temperature, etc.) from those for which the biradicals are observed. Thus, it would be desirable to measure the HFC constants of biradical termini directly with a minimum perturbation of its structure and experimental conditions.

We report here that a combination of spin-trapping and TR ESR techniques can provide the HFC constants of interest for monoradical structures which closely resemble the biradicals of interest. The approach employed is based on the selective scavenging of one of the odd electron's sites of a biradical, while leaving the other site intact. The remaining radical center is an excellent model for its (weakly interacting) counterpart in the biradical structure. At the same time, this approach results in a less complicated and much better resolved ESR spectrum which allows the direct and accurate measurement of the HFC constants. The applicability of the method is demonstrated for acyl-alkyl and acyl-benzyl polymethylene biradicals with bromotrichloromethane,  $\text{BrCCl}_3$ , as a selective scavenger of the acyl moiety. The benzylic hyperfine splittings thus obtained are compared to those for benzyl and 1-phenylpropyl radicals formed in the photolysis of corresponding linear ketones.

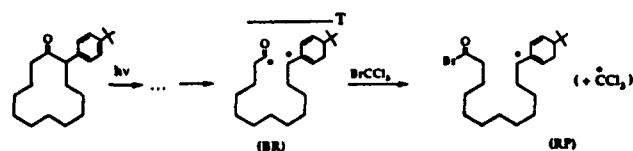
## Experimental Section

1-Phenyl-2-butanone, spectrograde or HPLC grade benzene (Aldrich), and triacetin (Janssen Chimica) were used as received.

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## SCHEME I



The syntheses of 2,2,12-trimethylcyclododecanone and 2-phenylcycloalkanones have been described previously.<sup>6,21</sup> 4-Phenylhexan-3-one was synthesized by alkylating 1-phenyl-2-butanone employing KH and  $\text{C}_2\text{H}_5\text{I}$  in THF and was purified by column chromatography on silica gel (hexanes and ethyl acetate eluting solvents). Capillary GC, GC/MS,  $^1\text{H}$ , and  $^{13}\text{C}$  NMR were used to characterize the products. No evidence of any compound with alkylation at the 3 position was observed.

Typically, a 10–15 mM solution of ketone in benzene was employed. 2-Phenylcycloalkanones were photolyzed in the presence of 45 mM  $\text{BrCCl}_3$ . For 2,2,12-trimethylcyclododecanone, 17 mM  $\text{BrCCl}_3$  in benzene was added to a 90 mM solution of the ketone. After purging with argon for 20 min the solutions were photolyzed (308-nm light (XeCl) of a Lambda Physik EMG 100 excimer laser) in a quartz flow cell (1-mm thick) positioned in the rectangular cavity of an X-band ESR spectrometer (Bruker, ER 100D). Direct detection of ESR signals without magnetic field modulation was employed. The output of the MW bridge broadband preamplifier (6.5 MHz) was fed into the boxcar averager and signal processor (PAR, Models 4420 and 4402). Operations of the laser and the boxcar were synchronized using the output of a fast photodiode as a triggering signal for the boxcar averager. The estimated deadtime for this configuration is ca. 200 ns and is taken into account in the integration windows indicated in the figure captions. Note that the TR CW ESR spectra are detected as true absorption and emission signals unlike conventional first derivative spectra in experiments with magnetic field modulation. Further details of the experimental setup have been described elsewhere.<sup>22</sup>

FT ESR spectra were detected employing a Bruker ESP-380 pulsed ESR spectrometer equipped with a 1 kW TWT amplifier (90° pulse length—16 ns) with a LeCroy 9450A oscilloscope as a fast digitizer (400 Ms/s sampling rate). The solutions were either static or flowing through a 4 mm o.d. quartz cylindrical cell.

A Pascal program was written for ESR spectra simulations. A conventional  $Q^{1/2}$  dependence of line intensities was used<sup>23,24</sup> with  $Q$  being the  $S-T_0$  mixing frequency. The contribution of only one of the two radicals in a radical pair RP is retained, since one radical usually prevails in the experimentally observed spectra. The lines in the calculated spectra have a Lorentzian shape with the same full width at half maximum (fwhm). In certain cases a three-point smoothing of the recorded spectra was used for clearer presentation, while the original spectra were used for simulations.

## Results and Discussion

Scheme I illustrates the relevant processes, initiated photolytically, in the case of 2-(*p*-*tert*-butylphenyl)cyclododecanone; they are common to all the cyclic ketones studied. Upon photoexcitation, the ketone, after intersystem crossing from the excited singlet state, undergoes  $\alpha$ -cleavage from its triplet state and forms a triplet acyl-benzyl biradical (BR, Scheme I).<sup>25</sup> The latter possesses a characteristic ESR spectrum (Figure 1) which displays alternating emissive and absorptive lines.<sup>26</sup> The spectrum is asymmetric due to the difference in  $g$ -factors of the two radical sites. The ESR lines are broadened and shifted as compared to the spectra of corresponding monoradicals (cf. Figure 3) as a result of an interaction of the two unpaired electron spins. Thus, for ESR spectra of biradicals, especially those possessing an acyl radical terminus, it is almost impossible to measure the hyperfine splittings directly and accurately.

Acyl radicals are known to efficiently abstract bromine from  $\text{BrCCl}_3$ .<sup>27</sup> Since in many cases the reactivity of biradical sites and the same sites in monoradicals is very similar, as, e.g., in hydrogen atom abstraction from mercaptans,<sup>12</sup>  $\text{BrCCl}_3$  is expected to serve as an efficient scavenger of the acyl terminus of biradicals such as the one shown in Scheme I. Moreover, the rate constant for reaction of a benzylic radical center with  $\text{BrCCl}_3$  is expected to be orders of magnitude smaller than for reaction of the acyl terminus with  $\text{BrCCl}_3$ . The rate constants reported for similar radicals are  $2.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  for benzoyl radical at room temperature<sup>27</sup> vs  $1.07 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  for benzyl (room temperature<sup>34</sup>) and  $2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  for 1-phenylethyl radicals ( $80^\circ \text{C}^{31}$ ). Thus, proper control of the concentration of  $\text{BrCCl}_3$  is expected to allow the selective scavenging of the acyl terminus of acyl-benzyl biradicals. A qualitatively similar situation should pertain to the scavenging of acyl-alkyl biradicals.

Thiols<sup>28</sup> and  $\text{BrCCl}_3$ <sup>6-8</sup> have been used as biradical scavengers to induce nuclear polarization (CIDNP) or to enhance  $^{12}\text{C}/^{13}\text{C}$  isotope separation in the products of cycloalkanone photolysis. These results, together with the NMR product analysis in the experiments with  $^{13}\text{C}$  labeled compounds,<sup>8</sup> suggest that in the presence of  $\text{BrCCl}_3$  the acyl-benzyl biradical (Scheme I) is transformed into a radical pair (RP) of substituted benzylic and  $\text{CCl}_3$  radicals as a result of Br atom abstraction by the acyl terminus. Preliminary ESR results<sup>22</sup> support this assumption. As shown below, the elimination of biradical nature of the intermediates produced by photolysis of a series of ketones in the presence of  $\text{BrCCl}_3$  leads to ESR spectra of the corresponding monoradicals with well-resolved hyperfine structure. The ketones and corresponding radicals studied are shown in Scheme II.

To test the proposed approach, consider (Scheme II) the photolysis of 2,2,12-trimethylcyclododecanone (1) which yields the radical (2). The latter possesses two sets of equivalent nuclei with relatively large HFC constants that are expected to make its ESR spectrum simple and unambiguous. In addition, the HFCs for a variety of alkyl radicals under different conditions reported in the literature<sup>29</sup> can be used for comparison and as a check of the validity of the proposed approach. The spectrum detected when 1 was photolyzed in the presence of 17 mM  $\text{BrCCl}_3$  is shown in Figure 2a. Although a higher reactivity is expected for the acyl radical center toward  $\text{BrCCl}_3$ , alkyl radicals are also known to react with  $\text{BrCCl}_3$ ,<sup>30,31</sup> so a certain amount of the alkyl terminus is probably scavenged. Indeed, at higher  $\text{BrCCl}_3$  concentrations ( $\geq 45 \text{ mM}$ ) the ESR signal disappears completely. This demands that the signal be detected at relatively short delays after the laser flash and leads to line broadening in the observed spectrum. Strong electron spin polarization observed (low field lines in emission, high field in absorption, E/A) is essential in CW TR ESR experiments to achieve good sensitivity and is fortunately often the case for photolytically generated short-lived radicals. It is interesting to note, however, that polarization possessed by radical (2) and other radicals formed in similar reactions is generated in the preceding biradical, with polarization generated in secondary pairs by RPM being considerably smaller.<sup>26</sup> This fact combined with fast relaxation of  $\text{CCl}_3$  radical can explain why the latter is not observed in the spectrum of Figure 2a and other spectra reported here. Detection of  $\text{CCl}_3$  radical by TR ESR has been reported for systems involving either strongly polarized radicals<sup>22</sup> or high concentrations of equilibrated  $\text{CCl}_3$  radicals.<sup>42</sup>

Comparison of the experimental spectrum with the simulated spectrum (Figure 2b) shows some differences of relative line intensities in the central portion of the spectra. This is probably due to some triplet mechanism (TM) net absorptive contribution to the experimental spectrum (E/A<sup>0</sup> pattern is observed) and is similar to the case of di-*tert*-butyl ketone photolysis.<sup>32</sup> The HFC constants obtained from the simulation [ $A(\text{CH}_3) = 22.88 \pm 0.1 \text{ G}$ ,  $A(\text{CH}_2) = 18.10 \pm 0.15 \text{ G}$ ] are somewhat different from those

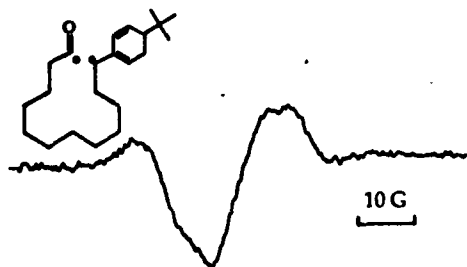
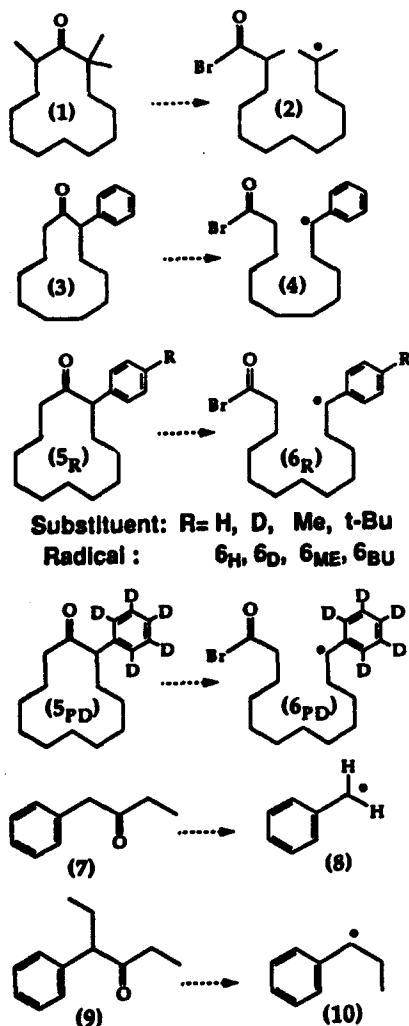


Figure 1. Experimental ESR spectrum of biradical (BR) (Scheme 1) obtained during the photolysis of ketone ( $S_{BU}$ ) with an integration window 0.2–0.5  $\mu$ s after the laser flash.

## SCHEME II



for 2-methylpent-2-yl radical [ $A(\text{CH}_3) = 22.2$  G,  $A(\text{CH}_2) = 17.8$  G].<sup>33</sup> Despite these differences the comparison leaves no doubt about the assignment of the experimental spectrum to the radical 2. This result supports the reaction mechanism of Scheme I and demonstrates that the proposed approach can indeed provide the information about hyperfine splittings of interest.

In the case of 2-phenyl substituted cyclic ketones (3,  $5_R$ , and  $5_{PD}$ , Scheme II) the variation of scavenger concentration in the range 8 mM–1 M does not lead to significant changes in the spectra observed, indicating a much smaller rate of Br atom abstraction by the benzylic terminus<sup>31,34</sup> compared to that for the alkyl terminus of biradical 2. All spectra observed show a similar E/A polarization pattern. The experimental spectrum of radical ( $6_{BU}$ ) obtained on the photolysis of ketone ( $S_{BU}$ ) and the simulated spectrum are shown in Figure 3. The presence of a *tert*-butyl substituent in the para position of the phenyl ring simplifies the

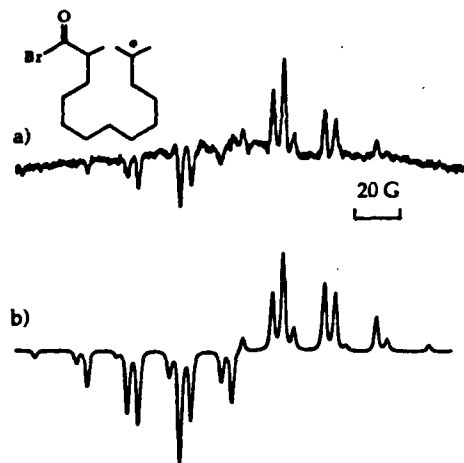


Figure 2. (a) Experimental ESR spectrum of radical (2) obtained during the photolysis of ketone (1) in the presence of  $\text{BrCCl}_3$  with an integration window 0.4–0.9  $\mu$ s after the laser flash. (b) Simulated spectrum. Lines have Lorentzian shape with fwhm = 1.2 G. HFC constants determined are  $A(\text{CH}_3) = 22.88 \pm 0.1$  G,  $A(\text{CH}_2) = 18.10 \pm 0.15$  G.

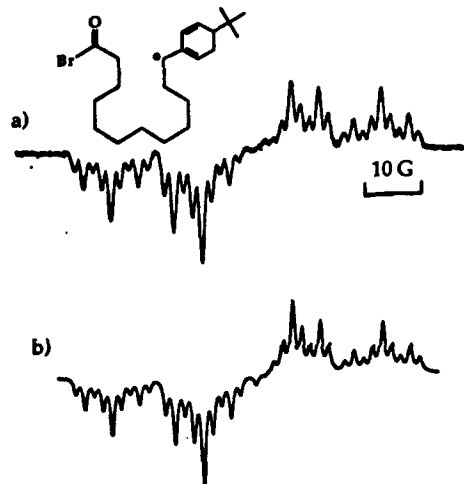


Figure 3. (a) Experimental ESR spectrum of radical ( $6_{BU}$ ). Integration window 0.7–1.2  $\mu$ s. (b) Simulation: lines are assumed to have Lorentzian shape with fwhm = 0.9 G. The HFC constants determined are shown in Table I.

analysis of the spectrum. The major quartet feature of the spectrum shows that the splittings due to  $\alpha$  and  $\beta$  hydrogens are identical within the accuracy of the measurement. The triplet of triplets feature of the spectrum readily allows computation of the values of the HFC constants for ortho and meta hydrogens. The HFC constants evaluated are summarized in Table I.

For the radical ( $6_{ME}$ ) with a *p*-methyl substituent in the phenyl ring, the HFC pattern is more complicated (Figure 4a), but nevertheless its simulation is unambiguous (Figure 4b) and yields accurate values of hyperfine splittings. Despite the high spectral resolution achieved, the splittings of  $\alpha$  and  $\beta$  hydrogen atoms cannot be distinguished. The same is true for the two nonequivalent ortho protons (*vide infra*).

The ESR spectra of radicals (4) and ( $6_H$ ), produced by scavenging of biradicals generated in the photolysis of 3 and  $5_R$ , coincide experimentally as expected, since they differ only in the number of methylene groups in long alkyl chain. The spectrum of radical (4) is shown in Figure 5 together with its simulation. A more complicated hyperfine pattern was observed for radical  $6_D$ . This feature prevents an accurate evaluation of HFC constants for ring hydrogens, but the splittings of  $\alpha$  and  $\beta$  hydrogens could still be determined with reasonable accuracy (Table I).

When all ring hydrogens are substituted by D atoms (radical  $6_{PD}$ ) the structure of the ESR spectrum collapses into four

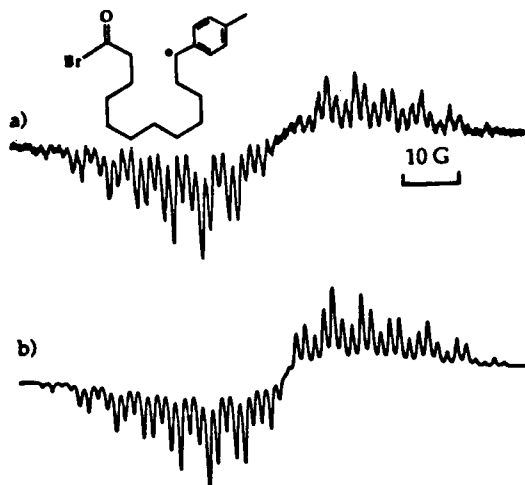


Figure 4. (a) Experimental ESR spectrum of radical ( $6_{ME}$ ) obtained with integration window 1.9–2.2  $\mu$ s. (b) Simulation with fwhm = 0.6 G for Lorentzian lines.

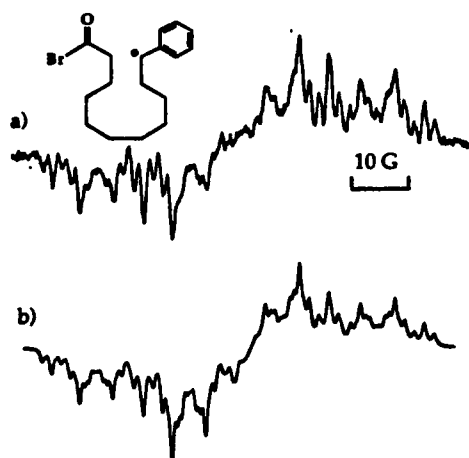


Figure 5. (a) Experimental ESR spectrum of radical (4) obtained with integration window 0.7–1.2  $\mu$ s. (b) Simulation with fwhm = 0.9 G for Lorentzian lines.

TABLE I: Absolute Values of HFC Constants Evaluated for Benzylic Monoradicals Formed upon Trapping of Corresponding Acyl-Benzylic Biradicals

radical	$A_\alpha$	$A_\beta$	$A_p$	$A_{CH_3}$	$A_\alpha$	$A_\beta$	uncertainty <sup>a</sup>
4, $6_H$	4.94	1.68	5.89		16.31	16.31	$\pm 0.15$
$6_D$	(4.94)	(1.68)	(0.91 <sup>*</sup> )		16.31	16.31	$\pm 0.15$
$6_{DD}$	(0.76 <sup>*</sup> )	(0.26 <sup>*</sup> )	(0.91 <sup>*</sup> )		16.31	16.31	$\pm 0.15$
$6_{ME}$	4.95	1.68		6.35	16.04	16.04	$\pm 0.1$
$6_{BU}$	4.91	1.66			16.00	16.00	$\pm 0.15$

<sup>a</sup> For the splittings of  $\alpha$  and  $\beta$  hydrogens the uncertainty indicated is for the sum  $A_\alpha + 2A_\beta$ , while the deviation of individual splittings can in principle be ca. 2 times larger. Splittings shown in the parentheses cannot be evaluated, and the corresponding splittings for radicals (4,  $6_H$ ) were used in the simulations. HFC constants of deuterons are marked with an asterisk and were calculated assuming  $A_H/A_D = 6.515$ .

broadened lines (Figure 6). The splittings of ring deuterons used in the simulation were recalculated from those of radical ( $6_H$ ) assuming that the ratio of hyperfine splittings of H and D atoms is determined solely by their magnetogyric ratios ( $\gamma_H/\gamma_D = 6.515$ ). The values of  $\alpha$  and  $\beta$  HFCs are given by the splitting in the observed quartet.

Inspection of Table I shows that while the splittings of ring hydrogens are essentially experimentally indistinguishable for all the radicals studied, the values of  $\alpha$  and  $\beta$  HFCs for benzylic radicals with methyl and *tert*-butyl substituents in the phenyl ring are clearly lower than for the four other radicals. This difference is reproducible and exceeds the experimental uncertainty. In fact, this observation is in good agreement with the

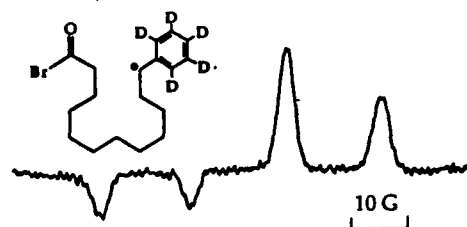


Figure 6. Experimental ESR spectrum of radical ( $6_{PD}$ ) obtained with integration window 0.7–1.2  $\mu$ s. The lines are inhomogeneously broadened due to unresolved deuterium hyperfine splittings.

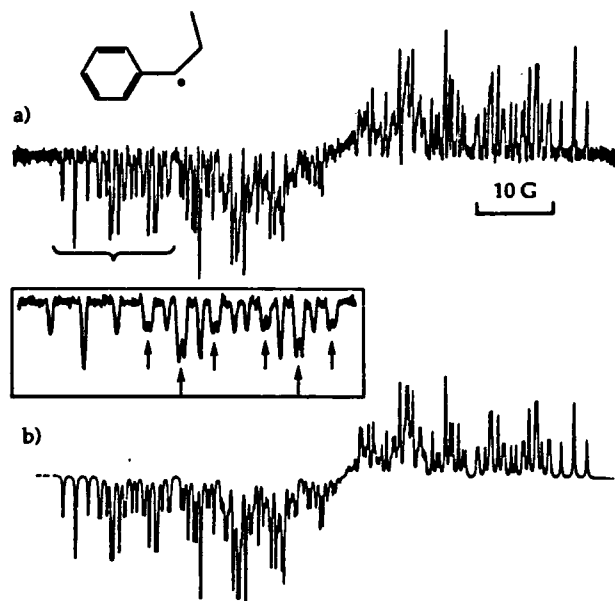

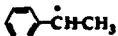





Figure 7. (a) Experimental ESR spectrum of 1-phenylpropyl radical (10) detected with the integration window 0.9–1.4  $\mu$ s upon photolysis of ketone (9) in triacetin. The inset shows the expanded portion of the spectrum indicated with a parenthesis. The arrows point to the apparent doublets due to nonequivalence of the two ortho hydrogens (see text for discussion). (b) Simulated spectrum. Lorentzian lines have fwhm = 0.15 G. The splittings evaluated are shown in Table II.

systematic study of the influence of different substituents upon the  $\alpha$ -hydrogen HFCs of substituted benzylic radicals reported in the literature.<sup>35–37</sup> The presence of a methyl or *tert*-butyl group in the para position leads to higher delocalization of the unpaired electron away from the benzylic position and causes extra stabilization of the benzylic radical. The delocalization leads to a smaller spin density at the benzylic carbon and thus to a decrease in  $\alpha$  and  $\beta$  hyperfine splittings, since both are proportional to its value.

An interesting issue involves the comparison of the HFC constants obtained for scavenging of biradicals with those for small structurally similar monoradicals. As far as we know, HFCs of 1-phenylalkyl radicals have been reported only for the simplest members, i.e., the benzyl and 1-phenylethyl radicals. For longer alkyl chains the splittings of  $\beta$  protons can vary somewhat from those of the simpler monoradicals. A well-resolved spectrum of radical 10 is observed when ketone 9 is photolyzed in triacetin (Figure 7a) or benzene. Its simulation (Figure 7b) reveals that the two ortho protons are not equivalent since their splittings are distinctly different. This feature is readily observable in the inset of Figure 7, where the apparent doublets indicated with arrows are in fact the result of two different ortho splittings. The same observation has been reported in the literature for other substituted benzylic radicals (Table II). The difference of ortho and ortho' splittings is ca. 0.25 G which means that the rotation interchanging the two ortho protons is slower than ca. 1  $\mu$ s, i.e., the two splittings would be averaged by a rotation that occurred on a shorter time scale. The activation energies and preexponential factors of this

TABLE II: Absolute Values of HFC Constants of Several Small Substituted Benzylic Radicals

radical	$A_o$	$A_m$	$A_p$	$A_a$	$A_\beta$	solvent	ref
	5.12	1.76	6.13	16.23		benzene, rt	a
	4.81	1.69	5.86	16.34	17.63	ethylbenzene, rt	[40]
	5.08						
	4.81	1.69	5.88	16.13	16.48	benzene, 303 K	[41]
	5.08						
	4.80	1.68	5.89	16.13	16.70	triacetin, rt	a
	5.07						
	4.83	1.68	5.89	16.18	16.76	benzene, rt	a
	5.06						

\* This work. The uncertainty for all splittings measured is  $\pm 0.05$  G.

rotation have been reported in the literature for several benzylic radicals<sup>38,39</sup> and correspond to a reorientation time of 0.1–1 ms at room temperature. Such slow rotation is due to the interaction of p-orbital of the unpaired electron with the  $\pi$ -system of the phenyl ring which stabilizes the planar geometry of the benzyl fragment.<sup>38</sup> Although the same holds true for other benzylic radicals studied in this work, the difference of the two ortho splittings (0.25 G) is much smaller than the line width of the spectra shown in Figures 3–6 (0.6–0.9 G) and thus cannot be observed. The hyperfine splittings for radicals 8 and 10 were obtained by both FT TR ESR and CW TR ESR experiments. The values coincide within the experimental error and are summarized in Table II together with the literature data for structurally similar radicals.

A comparison of Tables I and II shows that, although the hyperfine splittings for the two series are similar, they do not match exactly, especially for the  $\beta$ -hydrogens. This is not surprising since the splittings of  $\beta$  hydrogens are caused by hyperconjugation and depend considerably upon the angle between the orbital of the unpaired electron and the C–H bond. Increasing the bulk of the alkyl substituent in the  $\alpha$  position alters its steric interaction with the benzylic fragment and diminishes the splittings of  $\beta$  hydrogens (Tables I and II). Therefore, because of these conformational effects, which may be subtle, small benzylic monoradicals may not serve as accurate models for the corresponding radical sites in biradicals. Thus, while the ESR spectra of small radicals usually show much better spectral resolution, the proposed approach based on the scavenging of one of the biradical termini provides a direct way to measure the HFC constants of the other with a high accuracy and with a local molecular conformational structure that is expected to be very similar to that of the biradical. We note, however, that this approach is based on the assumption that electron spin interactions have no influence on the HFC constants. We are unaware of any reason to expect such influence in the systems investigated.

Finally, it should be noted that the application of the method considered is not limited to cases when considerable electron spin polarization is formed in the biradicals. Even if it is not the case, polarization may still be formed in the secondary radical pair, as, for example, in biradicals with much shorter chains separating the radical centers.<sup>24</sup> Thus, the role of a scavenger can be 2-fold: it should react selectively with one of the biradical termini and should supply a radical for a secondary RP. It is also feasible for strong TM polarization of biradical precursor to improve the S/N ratio in the spectra detected.

## Conclusions

The hyperfine splittings of one biradical terminus can be measured directly if the other terminus is scavenged with an appropriate spin trap. To be amenable to experimental investigation, such a measurement requires a selective scavenging of one of the biradical termini.  $\text{BrCCl}_3$  is a selective scavenger of the acyl terminus of the biradicals produced by photolysis of a

variety of cyclic ketones. Thus, transformation of the acyl–benzyl biradical into a substituted benzylic monoradical by photolyzing cyclic ketones in the presence of  $\text{BrCCl}_3$  (Scheme I) allows the ready evaluation of the HFC constants of benzylic biradical terminus. This procedure allows the evaluation of the HFC constants of excellent monoradical models of one of the biradical termini under the same experimental conditions as those employed for detection of biradical ESR spectra and does not require chemical syntheses of monoradical analog precursors. Splittings of several benzylic radicals were measured. Splittings of  $\beta$  hydrogens are clearly smaller for longer alkyl chains than for the simpler systems and presumably are the result of different steric restrictions. At the same time, all the spectra detected are in agreement with Scheme I. This lends further support for the assumption that the acyl moiety of the biradical efficiently abstracts Br atom from  $\text{BrCCl}_3$  and that the latter is a good scavenger of acyl-containing biradicals. The method is also effective for the selective scavenging of the acyl moiety of biradicals produced from  $\alpha, \alpha'$ -polymethylated cyclic ketones.

**Acknowledgment.** The authors thank the NSF and AFOSR for their generous support of this research.

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